

The Ultra-Violet Absorption Spectra of Certain Metallic Vapors and Their Mixtures

BY
DAVID VANCE GUTHRIE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BALTIMORE
1908



THE ULTRA-VIOLET ABSORPTION SPECTRA OF CERTAIN METALLIC VAPORS AND THEIR MIXTURES

By D. V. GUTHRIE

It has been found by one of the present writers that the absorption spectrum of a substance in the state of a vapor may be modified by the presence of another gas or vapor, in such a way as to indicate that there is some interaction between the molecules. In the case of iodine vapor¹ mixed with the vapor of ether or bisulphide of carbon of a given density, if the iodine is not present in excess we have the absorption spectrum which is characteristic of iodine solutions, i. e., a broad band which obliterates the blue-green and violet region. If a little more iodine is added we get at once the absorption spectrum of gaseous iodine, a spectrum containing hundreds of fine lines in the orange and yellow region. In other words, a given quantity of ether vapor of a given density is able to dissolve a given quantity of iodine, any excess of the latter substance existing in the gaseous state, that is, with its molecules unaffected by the other vapor.

A phenomenon of a different nature has been observed in the case of mercury vapor,² which has a strong absorption band at wavelength λ 2536. If the vapor is evolved in a vacuum, this band broadens rapidly on the less refrangible side, attaining a width of three or four hundred Angström units. There is little or no broadening in the other direction. If air, hydrogen, helium, nitrogen, or some other inert gas is present, the band broadens symmetrically at first, and, after acquiring a certain width, continues to increase only in the direction of longer wave-lengths.

The marked unilateral broadening of the mercury band is in itself a point of interest, and has been recently discussed by Larmor,³ who suggests that the unsymmetrical nature of the band may be due to the formation of loose molecular aggregates, which on account of mutual influence tend to vibrate in longer periods, and so give rise to the displaced part of the band. Another interesting case of this

¹ Wood, "Absorption Spectra of Solutions of Iodine and Bromine above the Critical Temperature," *Phil. Mag.*, **41**, 423, May 1896.

² Wood, *Astrophysical Journal*, **26**, 41, 1907.

³ *Astrophysical Journal*, **26**, 120, 1907.

kind is described by Lyman,¹ who finds an absorption band for oxygen in the extreme ultra-violet, which exhibits markedly unsymmetrical broadening. He applies Larmor's explanation to this band, observing that the conditions demanded by the theory exist in the case of oxygen. Since absorption bands of this character possess much interest, it is important to find whether they exist in case of other metallic vapors besides that of mercury.

OBJECTS OF INVESTIGATION

The present investigation was undertaken with the following objects in view.

1. To obtain the absorption spectra of certain metallic vapors, particularly in the ultra-violet region of the spectrum, where they have not been studied heretofore.

2. To observe the manner in which the absorption bands of each metal behave with increasing vapor-density.

3. To determine whether the absorption bands are affected in any way by the presence of a foreign substance.

APPARATUS AND METHODS

A small quantity of the metal to be studied was placed in a quartz bulb of 10 or 15 cc capacity, which was then exhausted and sealed. Quartz furnishes a very efficient material for use in examining the absorption of metals which volatilize at a temperature only moderately high, for, in addition to its transparency to ultra-violet light, it does not soften in the hottest flame of the ordinary blast lamp and so can withstand great pressures of the inclosed vapor. Prolonged heating of the bulbs in the flame of the Bunsen burner causes them to become incrustated on the outer surface with a material which was quite opaque to the shorter wave-lengths, apparently due to a sort of devitrification of the quartz. This could be removed, however, and the transparency of the bulb restored, by heating it to the softening point for a short time in the oxy-hydrogen flame.

As a source of light, a spark discharge between cadmium electrodes was used, a Leyden jar or a condenser being placed in parallel with the secondary circuit. This source furnishes a strong and fairly uniform continuous spectrum in addition to the scattered lines.

¹ *Astrophysical Journal*, 27, 87, 1908.

Whenever practicable the bulb was placed in a small air bath, formed of a piece of iron tubing not much greater in diameter than the bulb, with small holes cut in the sides to permit the light to pass through it. To determine the temperature in the air bath, a platinum-rhodium thermo-couple connected with a galvanometer reading the temperature directly up to 1400° was used. The highest temperature that could be secured in the air bath, heating it with two large burners with strong air blast, was about 700° , so when higher temperatures were necessary the bulb was heated directly in the flame of the burner or blast lamp.

In part of the work a quartz lens was used to bring the light from the spark, after passing through the quartz bulb, to a focus on the slit of the spectrograph, but usually it was found advisable to pass the light of the spark directly through the bulb into the instrument, the spark being distant 12 or 15 cm from the slit, and the quartz bulb about half-way between the two. The instrument used to photograph the spectra was a small quartz spectrograph. A device attached to the plate-holder enabled it to be raised by successive steps, so that the spectra could be photographed in succession as the temperature was raised and the vapor-density increased. The plates used were Seed's 26. The range of the spectrum which could be investigated extended from about λ 5200 to λ 2150.

OBSERVATIONS AND RESULTS

1. *Cadmium*.—Two absorption lines were found for cadmium, corresponding to the emission lines λ 2288.1 and λ 3261.2, the former being much the more prominent. As the vapor in the bulb increases in density the emission line of the spark λ 2288 appears bisected by a fine dark line, the widening of which finally obliterates the bright line entirely (Fig. 1). The dark band eventually attains a width of nearly 200 Å. U. The other absorption line makes its appearance in a different manner. There are two bright lines in the *Cd* spark spectrum at wave-lengths 3251 and 3261. As the vapor in the bulb increases in density the latter bright line gradually fades away, disappearing entirely at one stage. Its place is then taken by a dark line, which, however, never becomes very broad with the vapor-densities used in the present work. This apparent difference in the manner in which

the absorption line makes its appearance is, without doubt, to be attributed to the smaller dispersion of the quartz spectrograph for this region of the spectrum.

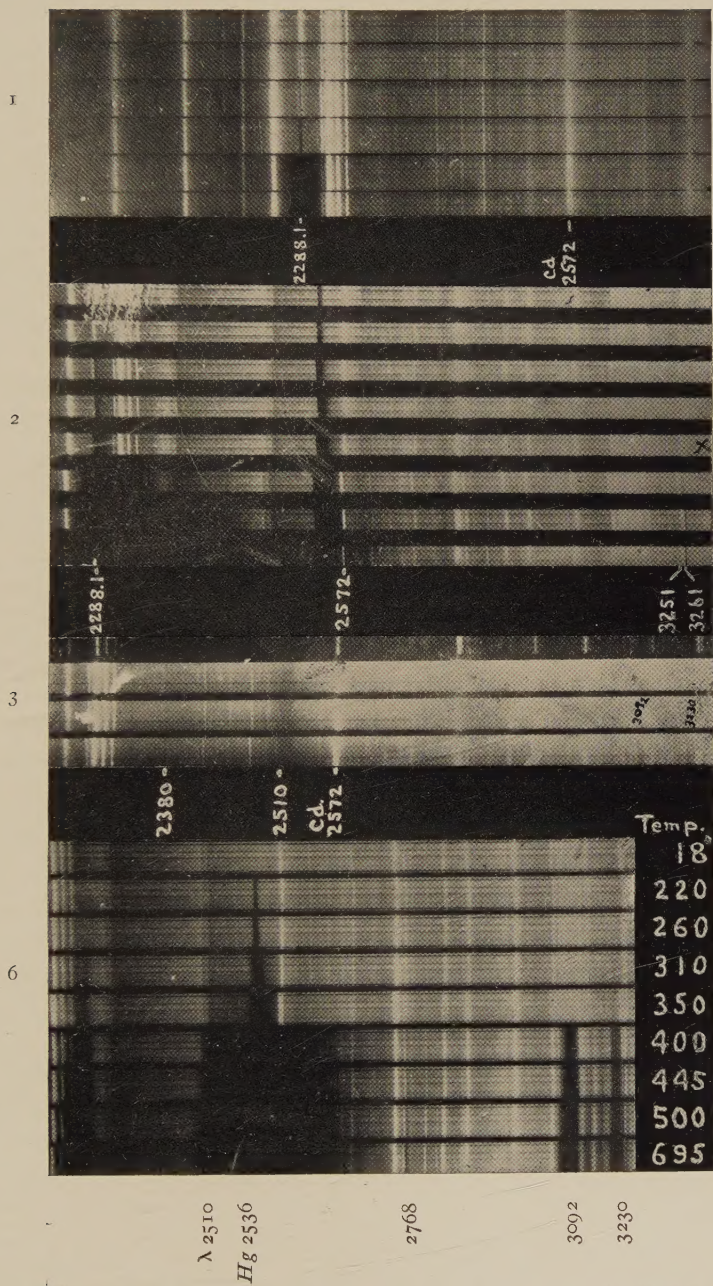
The absorption is relatively weaker than that of the line λ 2288, for the bright line λ 3261 is not obliterated until the λ 2288 line has attained the width shown in the lower two spectra of Fig. 1, Plate XX. The line λ 3261 is not shown in this figure, but it appears in Fig. 2. These two lines are the only ones in the cadmium spectrum which show any trace of absorption, though vapor of such density has been used that the line at λ 2288 broadened nearly to the cadmium line at λ 2572.

The manner of broadening of the absorption bands with increasing vapor-density was then studied. It was found that in a vacuum, no foreign substance being present with the cadmium, the band λ 2288 broadens perfectly symmetrically, the broadening amounting to considerably more than 100 A. U. on each side at the highest temperatures employed. It was found, however, in working with zinc in which a little cadmium was present as an impurity, that when mercury was added, this absorption band appeared to broaden only on the side toward the longer wave-lengths.

In order to determine whether this was really an effect of the mercury upon the cadmium, a bulb was prepared containing cadmium and a little mercury. In this case there was a marked unsymmetrical broadening of the absorption band at λ 2288 (Fig. 2). The band broadens a little on the more refrangible side, especially at the higher temperatures, but very much more on the less refrangible side. The emission line *reverses on the less refrangible side* first, instead of in the center as before, and the absorption band has extended almost as far as the emission line λ 2307 by the time the more refrangible edge of the emission line λ 2288 has entirely disappeared (Fig. 2). Mercury vapor, even when very dense, shows no absorption band at this point, though there is a fairly strong band at λ 2338 and another very broad one at λ 2140. Measurements on one of the negatives in which the band had attained a considerable width gave the following result:

More refrangible limit.....	λ 2415.1
Less refrangible limit.....	λ 2270.6
Mean.....	λ 2342.9

PLATE XX



showing that an apparent shift of the mean wave-length of the band from the position of the emission line (λ 2288.1) amounting to about 55 Å. U. has taken place. Similar measurements on negatives representing the absorption of pure cadmium showed that the distance of each limit of absorption from the emission line was the same, to within the limit of error of observation. The shift is of course only apparent, for the densest or heaviest part of the band remains in the position of the emission line.

This effect is all the more remarkable in that it forms a contrast to the behavior of the mercury band at λ 2536, which broadens unsymmetrically in vacuo, but symmetrically when a foreign gas is present. However, this effect, as clearly as that, affords an instance of a modification in the appearance and position of an absorption band of one substance resulting from the direct influence of a foreign substance. The absorption line at λ 3261 does not appear to be affected, showing no signs of asymmetry in either case. Its width, however, at the temperature available was too slight to enable any very definite conclusion to be drawn as to the effect of the mercury vapor upon it. It can be seen in the two lower spectra of Fig. 2. The gradual disappearance of the bright line does not show well in the enlargement. The spectrum in which it has just disappeared is marked with an α .

2. *Thallium*.—The absorption of thallium vapor was next investigated. It was found that when pure thallium was sealed up in an exhausted bulb and its absorption examined, three or four faint absorption bands were to be seen, appearing at about 400° and not becoming strong even at the highest temperatures. When now a little mercury was added to the thallium, and its absorption studied under the same conditions, a number of other absorption lines were brought out which did not appear at the highest temperatures with the pure thallium, while of the absorption bands obtained with the thallium alone, all except one *disappeared*. Thus the appearance of the absorption spectrum is entirely changed by the addition of the mercury. Further, it was found that the relative intensities of the absorption bands and the temperatures at which they first appear vary in a remarkable manner with the relative proportions of mercury and thallium.

The spark spectrum of thallium was photographed and most of the absorption lines were found to correspond to emission lines, though

there were a few which did not appear to coincide with any line in the spark spectrum. The absorption bands obtained with the pure thallium were (see Fig. 3):

a) A fairly sharp but faint absorption line corresponding to the emission line λ 2380. This is the only absorption line which appears under all conditions, both with and without the addition of mercury. In the present case, with pure thallium, it never became strong, even at the higher temperatures.

b) A broad and faint absorption band lying very near the emission line λ 2530.0 on the side of shorter wave-lengths. Its mean wave-length was about 2510.

c) A band resembling the last but even fainter, and bordering on the emission line at λ 3092 but lying on the less refrangible side of this line.

d) A group of three lines, faint and not very sharp, lying very close together and uniformly spaced. The middle component coincides with the emission line at λ 3230.

Though these bands appear at a comparatively low temperature (about 400°) they change very little either in width or intensity as the temperature is further increased, a circumstance which suggests that they may be due to some easily volatilized impurity.

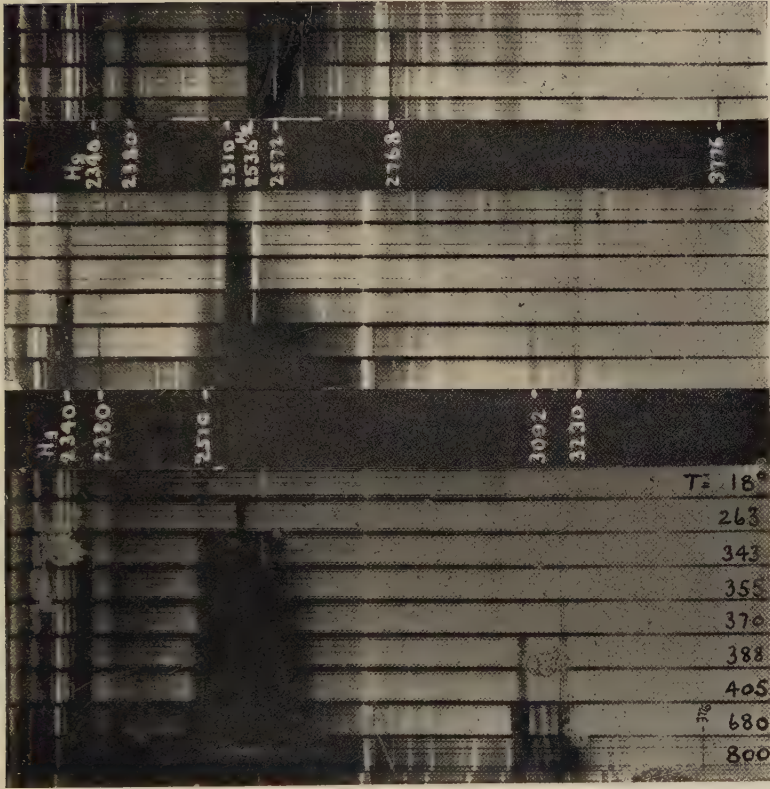
Some preliminary experiments with bulbs containing different proportions of thallium and mercury showed that with these mixtures absorption could be obtained in the case of several other lines, appearing at different temperatures in the different cases. In order to study the phenomenon quantitatively, a series of bulbs was examined containing definite amounts of thallium and mercury. First, 150 mg of thallium was weighed out and inserted in a bulb of about 10 cc capacity. Then, the amount of thallium being kept constant, six different amounts of mercury varying from 6 to 150 mg were tried with it. In the first case, although the amount of mercury was very small, the mercury absorption band at λ 2536 remaining quite narrow at the highest temperatures, this small quantity of mercury was sufficient to affect the absorption very markedly, bringing out very clearly absorption lines corresponding to the emission lines at λ 2580, λ 2768, and λ 3776 (Fig. 4, Plate XXI), and causing all the absorption bands found with the pure thallium except the one at λ 2380 to disappear.

PLATE XXI

4

5

7



λ 2510
Hg 2536

2768

3092
3230

3776

Absorption in the case of the line λ 2580 can be seen only when the amount of mercury in the bulb is small, for owing to the proximity to the mercury band λ 2536 it is hidden by the broadening of this band unless the band remains quite narrow. Previous experiments made by one of us have shown that the mercury band at λ 2536 even with very dense vapor expands only a few Ångström units on the short wave-length side, unless air or some other gas is present in which case it may extend almost as far down as the thallium band at λ 2510. With thallium and mercury, it apparently extends much farther down the spectrum; this change is only apparent, however, for we are dealing with two bands which fuse together when the vapor mixture is dense. The thallium band at λ 2510 broadens symmetrically, while the mercury band at λ 2536 broadens only on the side of longer wave-lengths. There are also indications, at high temperatures, of absorption corresponding to the line λ 2237.9 in one or two instances, when the amount of mercury present is small, this part of the spectrum being also obliterated in other cases by the strong absorption of mercury in the extreme ultra-violet. As the amount of mercury was increased, up to a certain point the absorption lines appeared at successively lower temperatures. Thus for the two cases where the amounts of mercury were 6 mg and 25 mg, the ratios of the amount of mercury to the amount of thallium being 1:25 and 1:2, the temperatures at which the absorption lines could be first detected were as follows:

Ratio Hg to Tl	λ 2380	λ 2580	λ 2768	λ 3776
1:25.....	600°	900° (est.)	600°	900° (est.)
1:2.....	400	700	400	500

The temperatures given are those of the air bath as indicated by the thermo-couple, except those over 700°, when the bulb was heated in the flame and the temperature estimated. For intermediate amounts of mercury the temperatures at which absorption appeared lay between these limits. As the proportion of mercury is still further increased beyond that in the second case above, the absorption lines do not appear at temperatures any lower than these.

This effect of mercury in bringing out absorption lines of thallium, which do not appear when pure thallium is examined under the same

conditions, appears to be quite analogous to some observations of Liveing and Dewar (*Proc. R. S.*, **27**, 132, 350, 1878), who found that the red line of lithium, λ 6103, could be obtained reversed only when both sodium and potassium were present. They found also, in studying the absorption of magnesium, that when sodium was present, a line at λ 5300 could be seen reversed and when potassium was present, two lines, at λ 6580 and λ 6475, these absorption lines being obtainable only with the mixtures. They suggest that

a very slightly volatile vapor may be diffused in an atmosphere of a more volatile metal, so as to secure a sufficient depth of vapor to produce a sensible absorption. This would be analogous to well-known actions which take place in the attempt to separate organic bodies of very different boiling points by distillation, where a substance of high boiling point is always carried over, in considerable quantity, with the vapor of a body boiling at a much lower temperature.

It seems quite probable that something of this kind occurs in the present case.

It has been mentioned that in the series of experiments just described in which 150 mg of thallium was used in the bulb and the amount of mercury varied, all of the absorption bands found with the pure thallium except λ 2380 disappear. The amount of mercury was now kept constant (about 150 mg) and the amount of thallium varied. The surprising result was obtained that as the amount of thallium in the bulb is increased above the amount used before, these absorption bands, which had disappeared in the former case, reappear, and as the amount of thallium is still further increased, they finally become very much stronger than with the pure thallium (Fig. 5 shows this effect). The most remarkable result was obtained with a bulb containing a large amount of thallium (Figs. 6 and 7). The bands just mentioned appear in this case at between 300° and 350°, being faint at first but rapidly becoming stronger, and finally at 400° and higher becoming very broad and intense, being almost as prominent as the mercury bands. The temperatures are recorded in the figures.

The circumstance which strikes one as most remarkable is that when there is but a small amount of thallium present (Fig. 4) the absorption lines at λ 2768 and 3776 are very conspicuous, while there is no trace of the strong bands λ 3092 and 3230. With a large amount of thallium we have the latter bands very conspicuous and little or

no trace of the former (Figs. 5, 6, and 7). This is especially noticeable in Fig. 7, in which the line at λ 3776 only appears in the lowest spectrum obtained at a temperature of about 800°. Whether this is a matter of the solution of thallium vapor in the vapor of mercury is a question. At the temperatures used it must be remembered that only a very minute proportion of the total amount of thallium present is vaporized in any case.

In addition to the bands which appeared in former cases, there are, in this case (Figs. 6 and 7), two strong bands lying between the bands at λ 3092 and the triplet at λ 3230, of which there were perhaps faint traces with the pure thallium, and also a number of fine lines lying near the band at λ 3230 on the less refrangible side, which are not represented on any of the former negatives. The wave-lengths of these absorption bands were measured. It was not possible to determine them very accurately, but the values given are correct to within a few tenths of an Ångström unit. For the two wider bands the limits of absorption were measured, while for the finer ones a setting was made on the middle of each, the average width being about 3 Å. U. The temperature in this case was 700°. The values obtained are as follows:

Limits of Absorption	Mean
3145.9 } 3166.6 }	3156.3
3179.1 } 3197.9 }	3188.5
Mean Wave-Length (width about 3.0)	
3267.9	3308.4
3279.7	3320.5
3289.4	3337.6
3297.4	3350.1

None of these absorption bands corresponds to any emission line. The triple line at λ 3230 appears shortly before the other bands, the most refrangible component being the strongest at first, though this is not the one that coincides with an emission line. The three lines merge into one and appear as a strong band at about 700°. The positions of the edges of these lines and of the band at λ 3092 were also

measured at different temperatures, the values obtained being as follows:

	Limits of Absorption	Mean
350°....	$\left\{ \begin{array}{l} 3220.2 \\ 3224.0 \end{array} \right\}$	3222.1
	$\left\{ \begin{array}{l} 3228.4 \\ 3231.5 \end{array} \right\}$	3229.9
	$\left\{ \begin{array}{l} 3236.8 \\ 3239.8 \end{array} \right\}$	3238.3
	$\left\{ \begin{array}{l} 3220.2 \\ 3225.7 \end{array} \right\}$	3223.0
400°....	$\left\{ \begin{array}{l} 3228.4 \\ 3233.4 \end{array} \right\}$	3230.9
	$\left\{ \begin{array}{l} 3236.8 \\ 3241.6 \end{array} \right\}$	3239.2
	$\left\{ \begin{array}{l} 3218.2 \\ 3262.1 \end{array} \right\}$	3240.2

* The three merged into one.

It will be observed that when the lines first appear, the middle component of the triplet coincides with the emission line at λ 3229.9, and that with increasing temperature they broaden at first only on the less refrangible side, though after merging into a wide band a slight extension toward the side of shorter wave-lengths is perceptible. For the band near λ 3092 the following values were obtained:

	Limits of Absorption	Mean
400°....	$\left\{ \begin{array}{l} 3091.9 \\ 3126.3 \end{array} \right\}$	3109.1
700°....	$\left\{ \begin{array}{l} 3081.3 \\ 3134.6 \end{array} \right\}$	3108.0

It is to be noticed that the band when it first appears just touches the position of the emission line at λ 3091.9 on its more refrangible edge, broadening, however, so as to cover it, the broadening being probably symmetrical.

The manner of broadening of the thallium absorption bands with increasing vapor-density was also investigated. Difficulty was experienced in getting the absorption bands to broaden sufficiently to draw definite conclusions as to their behavior, but finally on heating one of the bulbs containing thallium and mercury in the hottest flame of

the blast lamp, some of the bands brought out by the mercury attained a width of 15 or 20 Ångström units. The broadening of the bands λ 2768 and λ 3776 was found to be quite unsymmetrical, the extension on the side of longer wave-lengths being very much greater than on the opposite side, like that of the mercury band λ 2536, though not so marked as in that case. The appearance of these bands as they broaden also resembles that of the mercury band, as the limit of absorption remains very sharply defined on the more refrangible edge, but becomes very hazy and ill defined on the other side, on which the extension mainly occurs. This can be seen in Fig. 4. The line λ 2380 appears to broaden symmetrically. As already mentioned in a former part of the work, the lines at λ 3230 broaden toward the less refrangible side, while the wide band near λ 3092 probably broadens symmetrically.

The following measurements of the wave-lengths of the limits of absorption for the bands λ 2768 and λ 3776 clearly indicate the unsymmetrical character of the broadening for these wave-lengths. The observations are taken at three successive temperatures, the lowest being well above 700° and the highest in the hottest blast-lamp flame. They are estimated as 800°, 900°, and 1000°.

Temperature	Edges of Band	Mean	Emission Line at
800°	{ 2767.2 }	2768.2	{2768.1
	{ 2769.1 }		
	{ 2766.5 }		
900°	{ 2777.3 }	2769.9	{2768.1
	{ 2765.4 }		
	{ 2779.2 }		
1000°	{ 2779.2 }	2772.3	{2768.1
800°	{ Just visible }	3775.9	
900°	{ 3773.6 }	3776.5	
	{ 3779.3 }		{3775.9
	{ 3772.4 }		
1000°	{ 3786.3 }	3779.4	

As the unsymmetrical broadening of the cadmium band λ 2288 is caused only by the addition of mercury, it would be interesting to observe the behavior of these thallium bands with the pure thallium, but at the temperatures which could be attained in the present work

it was not possible to obtain these absorption bands except when mercury was added to the thallium.

It was thought possible that cadmium, which volatilizes at a much lower temperature than thallium, might have the same effect as mercury in bringing out thallium absorption bands, and so a mixture of thallium and cadmium was examined for absorption. The absorption of neither substance was modified by the presence of the other, however, the thallium absorption being the same as with pure thallium and the cadmium band λ 2288 broadening symmetrically and not showing the peculiar unsymmetrical effect caused by the addition of mercury.

Observations were also made to ascertain whether the addition of mercury to sodium has any effect upon the temperature at which the D lines appear in the absorption spectrum. For this purpose pure sodium and several mixtures of sodium and mercury in different proportions were sealed up in exhausted glass bulbs and the light from a carbon arc, after passing through the bulb contained in an air bath of which the temperature could be observed, was received on the slit of a spectroscope. No effect was observed, however, the temperature at which the D lines first appeared as absorption lines being practically the same in all cases.

3. *Other metals.*—The absorption of zinc was examined both with and without the addition of mercury. In no case did any trace of absorption appear in the region of the spectrum investigated, although zinc volatilizes at a much lower temperature than thallium. It seemed probable that results might be obtained with magnesium, which also volatilizes at a comparatively low temperature, and has several lines which are often seen reversed, but when heated the magnesium attacked the surface of the quartz, rendering it opaque, and making it impossible to work with this metal. The absorption of magnesium vapor was then investigated by passing the light of the cadmium spark through the vapor contained in a long porcelain tube, the ends of which were closed by quartz plates, which was heated by means of a Heraeus electrical furnace. Rather strong absorption was found corresponding to the emission line λ 2852.2, but nowhere else in the spectrum. In particular, visual observations revealed no trace of absorption for the lines of the *b* group, even at the highest

temperatures, which were probably well above 1000° . The influence of mercury was investigated, but its presence was found to have no effect on the absorption of the magnesium vapor.

The absorption of tin, of lead, and of bismuth was also investigated. As these metals volatilize at a higher temperature, though still lower than thallium, a little mercury was added in each case with the idea that it might help on absorption, as with thallium. No absorption was observed, however, with any of these metals.

SUMMARY OF RESULTS

The results of the foregoing investigation may be summarized as follows:

1. The absorption of cadmium vapor in the ultra-violet region of the spectrum was investigated and two absorption bands were found, one corresponding to the emission line at λ 2288, the other to λ 3261. Of these the former is much the more prominent.

2. The cadmium absorption band λ 2288 was found to broaden perfectly symmetrically when the pure cadmium was examined, but when mercury was added showed a marked asymmetry, broadening much more on the less refrangible than on the opposite side.

3. The absorption of thallium vapor was investigated, and with the pure thallium four absorption bands were found, two corresponding to the emission lines at λ 2380 and λ 3230 respectively, one lying near λ 2530, on the more refrangible side, and one lying on the less refrangible side of λ 3092.

4. With a moderate amount of thallium in the bulb all these bands (except λ 2380) disappear when mercury is added, but as the quantity of thallium present is increased they reappear, and finally become much stronger than with the pure thallium. On adding mercury other bands also appear which are not found with pure thallium. Among these are bands corresponding to emission lines at λ 2580, λ 2768, and λ 3776.

5. The behavior of these bands with increasing vapor-density was studied, and some of the bands, notably λ 2768 and λ 3776, showed a marked asymmetry, broadening chiefly on the less refrangible side.

BIOGRAPHICAL SKETCH

David Vance Guthrie was born on October 15, 1884, near Barter Brook in Augusta County, Virginia, being descended from a purely Scotch-Irish ancestry. He received his primary education at the Chamberlain-Hunt Academy, Port Gibson, Mississippi, and in 1899 entered Washington and Lee University, from which he graduated with the degree of A.B. in 1903. He received the degree of M.A. from the same university in 1904, having completed the entire courses of study there offered in the departments of mathematics, physics, chemistry, Latin, Greek, English, and philosophy. While at Washington and Lee University he received a scholarship in English, 1901, and in chemistry, 1902, the Young Scholarship in philosophy, and the Santini Prize Medal in 1903. He entered Johns Hopkins University in 1904, and while there has attended lectures in physics by Professor Ames, Professor Wood, and Dr. Whitehead, in physical chemistry by Professor Jones, and in mathematics by Dr. Cohen.

